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NEW ZEALAND

PATENTS ACT 1953

No.

Date

COMPLETE SPECIFICATION

IMPROVED PERSONAL SKIN CARE PRODUCTS CONTAINING
DIMETHYL DIALLYL AMMONIUM CHLORIDE/ACRYLIC
ACID-TYPE POLYMERS.

1. We, CALGON CORPORATION, a corporation duly organized and existing under the laws of the State of Delaware, United States of America of Route 60-Campbell's Run Road, Robinson Township, State of Pennsylvania, United States of America,

hereby declare the invention for which 1/ we pray that a patent may be granted to me/us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

C-1442

TITLE OF THE INVENTION

"IMPROVED PERSONAL SKIN CARE PRODUCTS CONTAINING
DIMETHYL DIALLYL AMMONIUM CHLORIDE/ACRYLIC ACID-TYPE
POLYMERS"

BACKGROUND OF THE INVENTION

5 The instant invention relates to improved personal
skin care products which contain at least one dimethyl
diallyl ammonium chloride (DMAAC)/ acrylic acid-type
polymer. These polymers impart a soft, silky feel to
the skin when present at low concentrations and are
compatible with anionic systems.

10 Numerous references disclose cosmetic and personal
care compositions such as shampoos, antiperspirant
formulations, anti-dandruff rinse conditioners, etc.,
which contain anionic and/or cationic polymers, an
active agent, surfactants, emollients and other
15 additives and preservatives commonly employed in the
industry. Pertinent references which relate to

DMDAAC/acrylic acid polymers or which disclose
cosmetic and personal care formulations containing
anionic and cationic polymers include:

- 5 1. US Patent 3,761,417, which is directed to
detergent compositions containing particle
deposition enhancing agents. More particularly,
this patent discloses detergent and personal use
toilet detergent bars containing water-soluble
10 particles such as antimicrobial agents, organic
surfactants and cationic polymers. Surfactants
are an essential ingredient of these compositions,
and DMDAAC is mentioned as a possible cationic
polymer.
- 15 2. US Patent 3,769,398, which discloses non-ionic
hair shampoo formulations containing an active
ingredient such as a betaine, sulfo betaine, amine
oxide or mixture thereof, a water soluble polymer
20 such as a polyethyleneimine-ethylene oxide or
propylene oxide polymer or a propoxylated
polyethyleneimine.
- 25 3. US Patent 4,329,335, which describes an
amphoteric, nonionic anti-dandruff shampoo
containing an active agent (1-imidazalyl-1-)
(chlorophenoxy-3, 3-dimethylbutane-2-one) and
amphoteric surfactants. DMDAAC is disclosed as a
30 preferred quaternized ammonium compound in this
patent.

4. Published European Patent Application No. 74,811, which discloses an anti-dandruff cream rinse conditioner containing zinc pyrithione, glucan guar gum, hydroxyethyl cellulose and a homopolymer of DMDAAC or a copolymer of DMDAAC and acrylamide.
5. US Patent 3,996,146, which discloses a shampoo formulation comprising from 0.05 to about 2.5%, by weight, of a cationic resin including quaternary polymers derived from dimethyl diallyl ammonium salts.
6. US Patent 4,040,984, which discloses polymers useful for preparing electroconductive paper which comprise quaternary diallyl dialkyl ammonium monomers and acrylic acid.
7. US Patent 3,912,808, which discloses a composition and method for waving or straightening hair using an aqueous solution of a reducing agent and a water soluble secondary or tertiary amine polymer or a polymer of diallyl amine or a quaternary polymer of diallyl dialkyl ammonium salts. This patent also discloses the use of dialkyl ammonium polymers which contain acrylamide or diacetone acrylamide. The use of dimethyl diallyl ammonium chloride/acrylic acid polymers is not disclosed or suggested.
8. US Patent 4,027,008, which discloses hair treating compositions which contain a water soluble secondary or tertiary amine polymer or a polymer of diallyl amine or a quaternary polymer of



diallyl dialkyl ammonium salts. This patent does not disclose or suggest the use of DMAAM acrylic acid polymers, and states that many widely used products for treating hair contain anionic surfactants which may inactivate cationic additives.

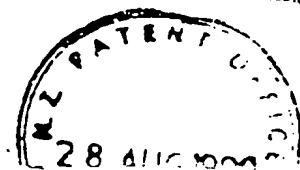
9. US Patent 3,986,825, which discloses the use of dialkyl diallyl ammonium polymers in cosmetic products, including copolymers of a dialkyl diallyl ammonium monomer and acrylamide or diacetone acrylamide. However, polymers containing these cationic moieties and acrylic acid are not disclosed or suggested.

In summary, though dialkyl diallyl ammonium polymers are widely used in cosmetic applications, the use of polymers containing a diallyl dialkyl ammonium monomer and acrylic acid is not known or suggested in the art. These polymers provide an increased level of cationic activity with unexpected compatibility in anionic systems.

DETAILED DESCRIPTION OF THE INVENTION

The instant invention is directed to a method for improving the feel of a personal skin care product, comprising adding to said product an effective amount of a polymer comprising:

- a) substantially 60 to 99%, based on total polymer weight, of a quaternary diallyl dialkyl ammonium monomer, wherein alkyl groups are independently selected from alkyl groups of 1



to 18 carbon atoms, preferably C_{12-14} , and wherein said quaternary diallyl amine ammonium monomer's counterion is selected from the group consisting of conjugate

of acids having an ionization constant greater than 10^{-13} , more preferably, selected from the group consisting of fluoride, bromide, chloride, hydroxide, nitrate, acetate, hydrogen sulfate, and primary phosphates; and

b) a polymer of the above described monomers, wherein the polymer weight, not an amine monomer, is selected from the group consisting of acrylic acid and methacrylic acid; wherein the weight average molecular weight of said polymer ranges from substantially 10,000 to 1,000,000.

The instant invention is also directed to personal skin care products which contain the above described polymer.

As used herein, the phrase "personal skin care product" includes, but is not limited to, hand and face lotions, soaps and creams, suntan lotions, bubble baths, shaving creams, antiperspirants and deodorants. The instant polymers impart a soft and silky feel to the skin when products containing them are used. The term "feel", as used herein, refers to a subjective measure of the smoothness and silkiness that a personal skin care product imparts to the skin when applied to the skin.



Personal skin care products generally comprise an active agent, such as a detergent or surfactant, conditioner, emollient, antimicrobial, antiperspirant and moisturizing agent. For example, active agents may include antimicrobial agents such as trichlorocarban (3,4,4'-trichloro carbanilide), triclosan (2,4,4'-trichloro carbonilide), triclosan (2,4,4'-trichloro-2'-hydroxy diphenyl ether), benzalkonium chloride, zinc phenosulfonate, zinc ricinoleate and the like.

Commonly used anti-perspirants include aluminum zirconium complex, aluminum chlorohydrate and the like.

Representative emollients, humectants and moisturizing agents include C₁₂-C₁₅ alcohol benzoates, sorbitol, glycerin, propylene glycol (PEG), lanolin, vegetable oils, mineral oils, isopropyl myristate, aloe vera, jojoba oil and the like.

Other cosmetically acceptable excipients that a personal care product formulation may contain are thickening agents, buffering agents and preservatives. Suitable water soluble preservatives are sodium bisulfite, sodium thiosulfate, ascorbate, benzalkonium chloride, glydant chlorobutanol, thimerosal, phenylmercuric borate, Dowicil 200 parabens, Tektamer 38(1,2-dibromo-2,4-dicyanobutane), benzyl alcohol, phenylethanol and the like. Suitable thickening agents are Cab-O-Sil M5 made by Cabot Corporation, sodium stearate, magnesium aluminum silicate, hydroxyethyl cellulose and the like. These agents may be present in amounts of from 0.05 to 50% by weight and preferably 1 to 5%. Suitable water

soluble buffering agents are alkali or alkali earth carbonates, phosphates, bicarbonates, citrates, borates, acetates, acid anhydrides, succinates and the like, such as sodium phosphate, citrate, borate, acetate, bicarbonate and carbonate. These agents may be present in an amount sufficient to maintain some optimum pH of the system in the range 2 to 9. As such, the buffering agent can be as much as 20%, on a weight basis, of the total composition. Additional active agents are fully described in U.S. Patent 3,986,825, which is incorporated herein by reference.

The instant polymers, in addition to imparting improved feel to skin, may enhance dispersion and improve the efficacy of functional ingredients in personal skin care products.

As used herein, the term "effective amount" refers to that amount of polymer required to improve the feel of the personal skin care product to which it is added. Generally, the instant polymers are added at a dosage ranging from substantially 0.1 active polymer solids to substantially 5 active polymer solids, based on the total weight of the product to which the polymer is added. Preferably, the dosage ranges from about 0.2 to about 3%, based on the total weight of the composition being treated and most preferably from about 0.5% to about 2.5%, based on the total weight of the composition being treated.

The quaternary diallyl dialkyl ammonium monomer comprises from substantially 0.1 to substantially 5% based on total polymer weight, while the anionic monomer comprises from substantially 1 to substantially 4%, based on total polymer weight.



weight. Preferably, the quaternary:anionic weight ratio is from about 95:5 to about 75:25, based on total weight of polymer. Thus, in the polymers of the present invention, the cationic moiety of the polymer is predominant while the anionic moiety of the polymer is minor. Additionally, other moieties may be present in the instant polymers.

An especially suitable polymer is that where the cationic portion is dimethyldiallyl ammonium chloride (DMAAC) or diethyldiallyl ammonium chloride (DEDAAC) and where anionic portion is acrylic acid. Preferably, the DMAAC/DEDAAC:acrylic acid weight ratio ranges from about 99:1 to about 60:40, most preferably from about 95:5 to 75:25, based on total polymer weight.

The polymers of the instant invention may have any molecular weight ranging from substantially 10,000,000, with the preferred molecular weight ranging from about 200,000 to about 5,000,000. The most preferred viscosity for the instant polymers ranges from about 4,000 to about 10,000 cps, as determined using a Brookfield LVF No. 4 spindle at 60 rpm. These polymers may be prepared using any conventional free radical polymerization technique, such as the technique disclosed by Butler and Angelo, "Journal of American Chemical Society," Vol. 79, p. 3128 (1957) or the technique suggested in U.S. Reissue Patent No. 28,543. These references are incorporated by reference into this specification.



The following example is not intended to limit the scope of this invention in any way.

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	<u>Ingredients</u>	<u>g./w./w.</u>
20	A. Deionized Water	41.90
	Sodium Lauryl Sulfate	25.50
	Sodium C ₁₄₋₁₆ Olefin Sulfonate ¹	10.00
25	Cerasynt M ²	0.40
	Cocamide DEA ³	2.00
	Cocamidopropyl Betaine ⁴	8.00
	B. MERQUAT 280 ⁵	2.00
30	C. Fragrance	0.50
	Tetrasodium EDTA ⁶	0.20
	D. Citric Acid	to pH 6.00
35	Sodium Chloride	to viscosity 2500 cps

Preparation Instructions

Heat water to 75°C. With moderate agitation, add the ingredients listed in Part A in the order stated, proceeding after each addition is uniform. Begin cooling and add MERQUAT 280 at 50°C. Continue mixing and cooling and add Part C at 45°C. Adjust pH to 6.0 with nitric acid. Add sodium chloride to increase viscosity to 2800 cps. Optionally, fragrances and dyes can be added.

1. Sodium laureth sulfate is C₁₄₋₁₆ olefin sulfonate sulfate is an anionic surfactant.
2. Cerasynt is ethylene glycol monostearate, available from Van Dyk & Co., Inc.
3. Cocamide DEA is coconut diethanolamine, available from Van Dyk and Co., Inc.
4. Cocamidopropyl betaine is a coconut amidopropyl betaine.
5. Merquat 280 is an 80/20 w/w polymer of DMDAAC and acrylic acid having a viscosity (Brookfield LVF #4 spindle @30 rpm) of 4,000-10,000 cp, and a weight average molecular weight of approximately 1,300,000, as determined by gel permeation chromatography, commercially available from Calson Corporation.
6. Tetrasodium EDTA is the sodium salt of ethlenediamine tetraacetic acid.

WHAT WE CLAIM IS:

1. ~~A method for improving the feel of a personal skin~~
care product, comprising adding to said product an
effective amount of a polymer comprising:
 - a. substantially 60 to substantially 99%, by
weight of said polymer, of a quaternary diallyl
dialkyl ammonium monomer, wherein alkyl groups
are independently selected from alkyl groups of
1 to 18 carbon atoms and wherein said quaternary
diallyl dialkyl ammonium monomer's counterion is
selected from the group consisting of conjugate
bases of acids having an ionization constant
greater than 10^{-13} ; and
 - b. substantially 1 to substantially 40%, by weight of
said polymer, of an anionic monomer selected from
the group consisting of acrylic acid and metha-
crylic acid; wherein the weight average molecular
weight of said polymer ranges from substantially
50,000 to 10,000,000, as determined by gel
permeation chromatography.
2. The method of Claim 1, wherein said alkyl group of
a) is C_{1-4} .
3. The method of Claim 1, wherein a) is selected from
the group consisting of dimethyldiallyl ammonium
chloride and diethyldiallyl ammonium chloride and
b) is acrylic acid.



4. The method of any one of Claims 1 to 3, wherein said effective amount ranges from substantially 0.1 to substantially 5%, by weight, of said product.
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5. The method of any one of Claims 1 to 4, wherein said product comprises an active agent and a surfactant.
6. The method of Claim 5, wherein said surfactant is anionic.
7. The method of any one of Claims 1 to 6, wherein said counterion is selected from the group consisting of fluoride, chloride, bromide, hydroxide, nitrate, acetate, hydrogen sulfate and primary phosphates.
8. A personal skin care product which comprises:
- a. an active agent;
 - b. an anionic surfactant;
 - c. a copolymer comprising:
 - 1. substantially 60 to substantially 99%, by weight of said polymer, of a quaternary diallyl dialkyl ammonium monomer, wherein alkyl groups are independently selected from alkyl groups of 1 to 18 carbon atoms and wherein said quaternary diallyl dialkyl ammonium monomer's counterion is selected from the group consisting of conjugate bases of acids having an ionization constant greater than 10^{-13} ; and
 - 2. substantially 1 to substantially 40%, by weight of said polymer, of a monomer selected from group consisting of acrylic acid and methacrylic acid; wherein said polymer has a weight average molecular weight ranging from substantially 50,000 to substantially 10,000,000, as determined by gel permeation chromatography.



9. The product of Claim 8 wherein 1. is selected from the group consisting of dimethyldiallyl ammonium chloride and diethyldiallyl ammonium chloride and 2. is acrylic acid.
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28 August 1890

Greta Gottlieb.

